Overtone vibrational spectroscopy and dynamics in H_2-H_2O complexes: a combined theoretical and experimental study

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H_2-H_2O

- H_2 most abundant molecule in interstellar medium (ISM), H_2O third (after CO)

- H_2-H_2O interactions important

  - collisions $\Rightarrow$ state populations of H_2O (maser)

  - complex formation?

  - H_2 formation on icy grains

- Infrared spectrum H_2-H_2O $|02^-) \leftarrow |00^+)$

  dimer lines observed, but not understood

H_2-H_2O

9D potential surface from Valiron *et al.* (2008)

$\Rightarrow$ 5D intermolecular potentials for various vibrational states of H_2/D_2 and H_2O/D_2O by averaging over monomer wave functions

VRT levels calculated for H_2-H_2O and D_2-H_2O ground states, and for H_2-H_2O $|02^-)$

Basis with $j_A \leq 10$ and $j_B \leq 8$

Symmetry group G_8 generated by P_{12}, P_{34}, E^*

Also H_2O $|02^-) \leftarrow |00^+)$ transition line strengths calculated

Calculation of VRT states

Hamiltonian

$$
\begin{aligned}
H &= \left[A j_{A_a}^2 + B j_{A_b}^2 + C j_{A_c}^2\right] + B j_B^2 - \frac{\hbar^2}{2\mu_{AB} R} \frac{\partial^2}{\partial R^2} R \\
&\quad + \frac{1}{2\mu_{AB} R^2}\left[J^2 + j_{AB}^2 - 2\boldsymbol{j}_{AB}\cdot\boldsymbol{J}\right] + V(R, \boldsymbol{\omega}_A, \boldsymbol{\omega}_B)
\end{aligned}
$$

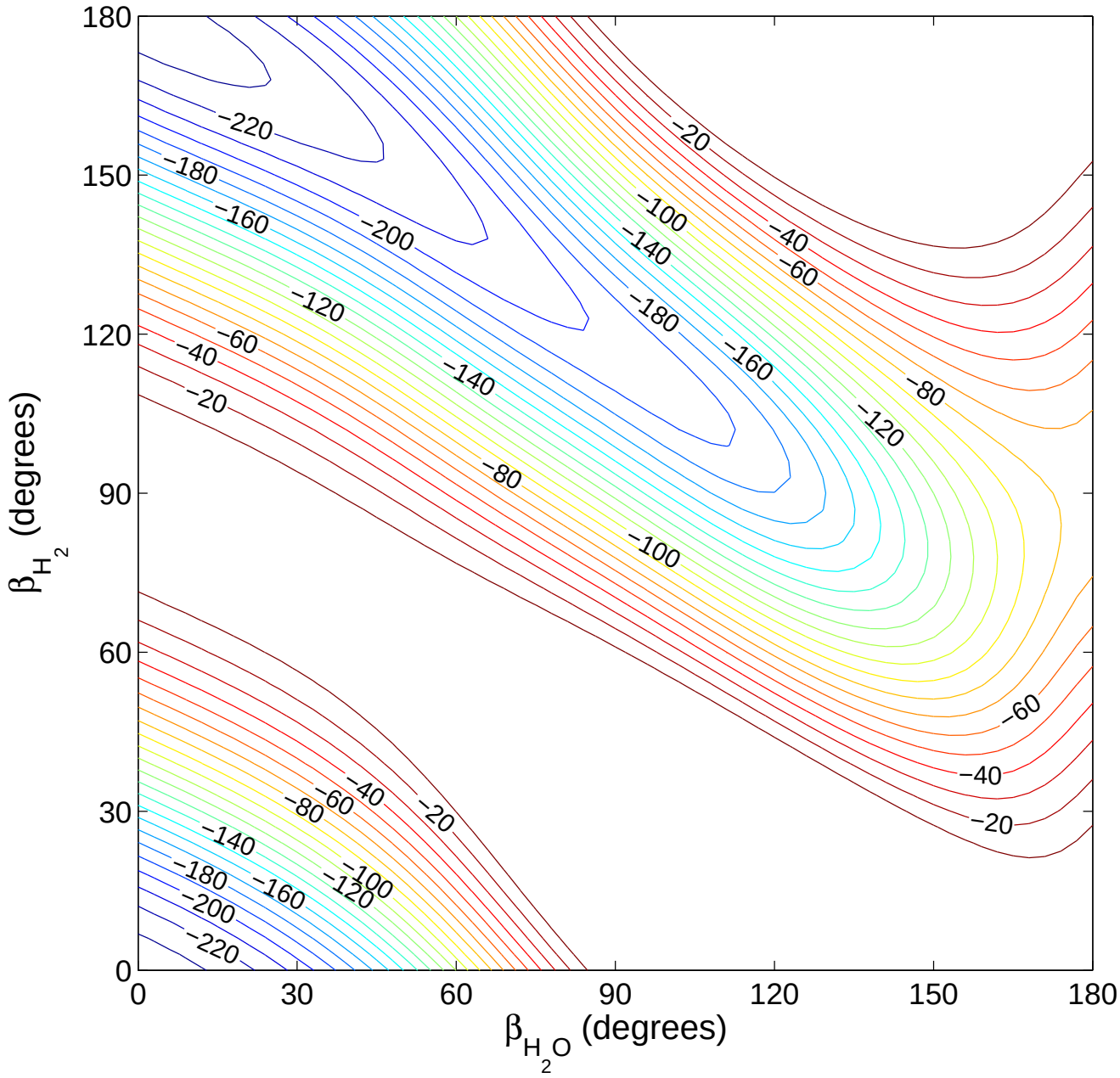
Analytic basis

$$
\chi_n(R) \sum_{m_A m_B} D^{(j_A)}_{m_A k_A}(\boldsymbol{\omega}_A)^* Y_{j_B, m_B}(\boldsymbol{\omega}_B)^* \langle\, j_A m_A; j_B m_B \mid j_{AB} K \,\rangle\, D^{(J)}_{MK}(\alpha, \beta, 0)^*
$$

contracted DVR for $\chi_n(R)$

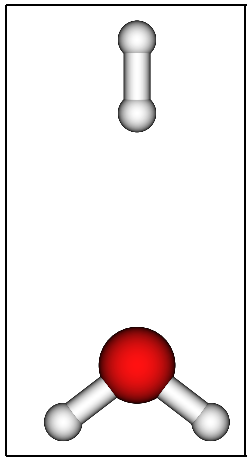
Basis adapted to irreps of PI group G_8

Potential surface

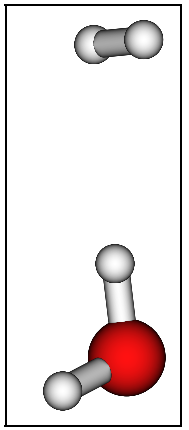


Minima

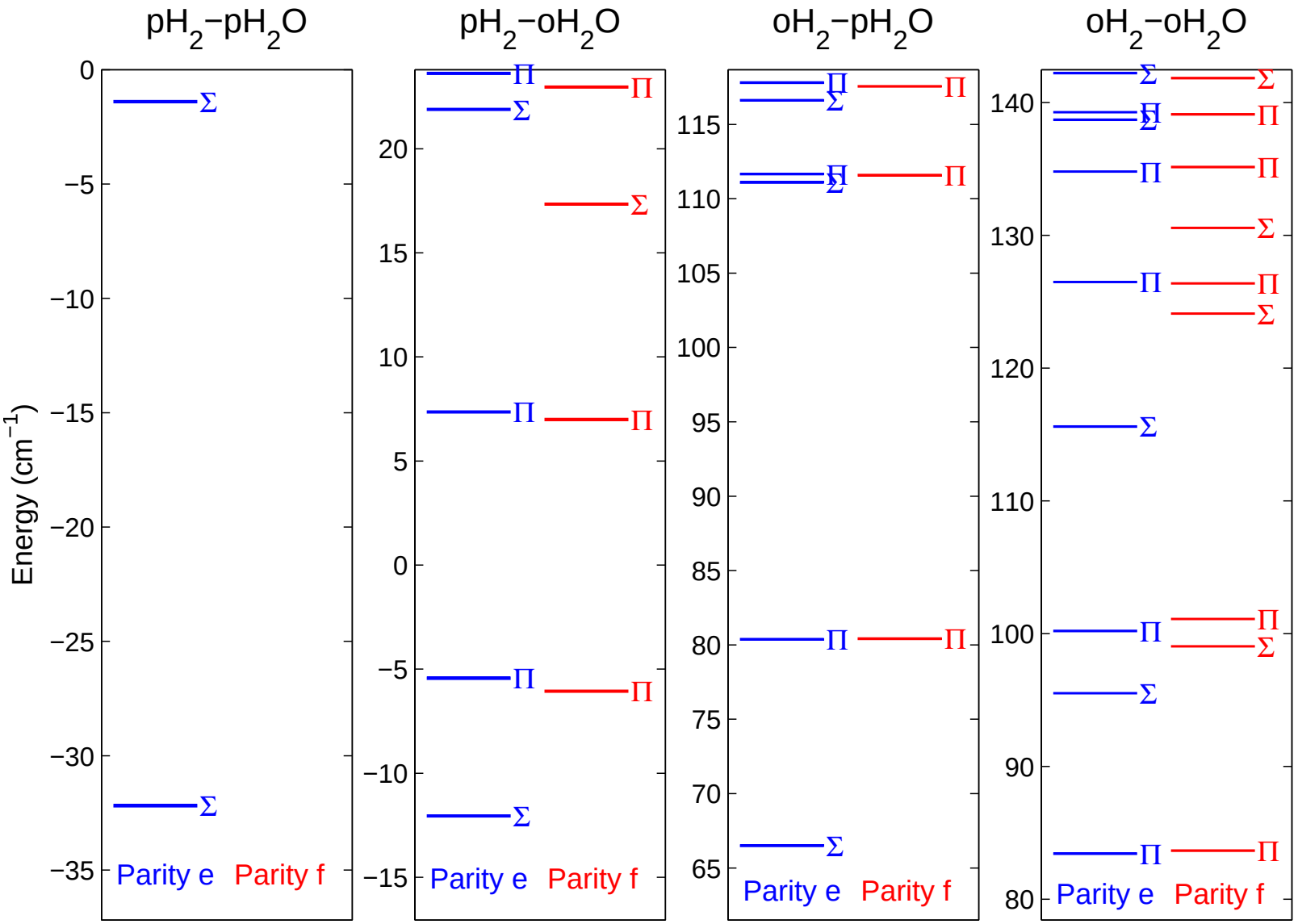
Global



Local

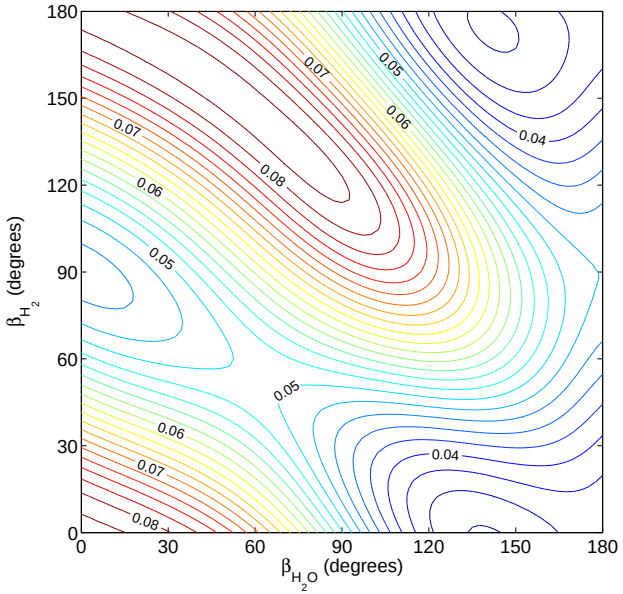


Calculated energy levels ($J = 1$)

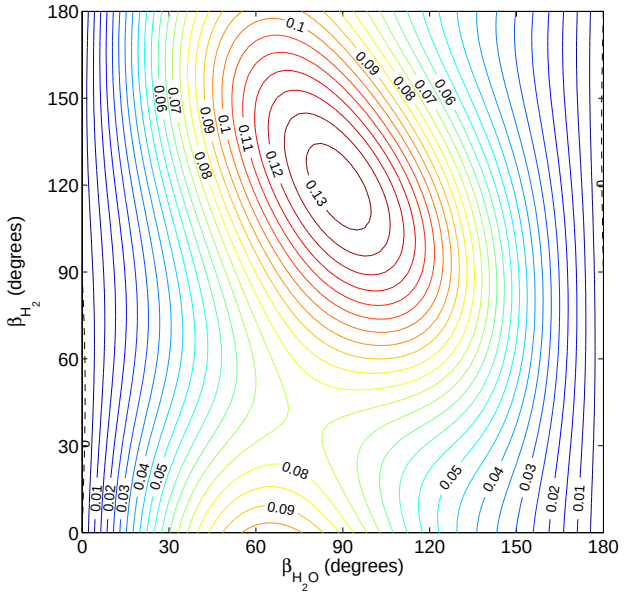


Wave functions ($J = 0$)

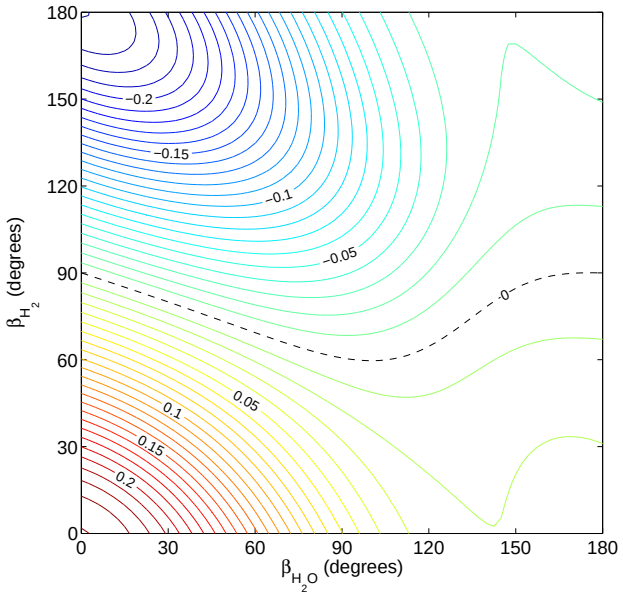
pH_2-pH_2O



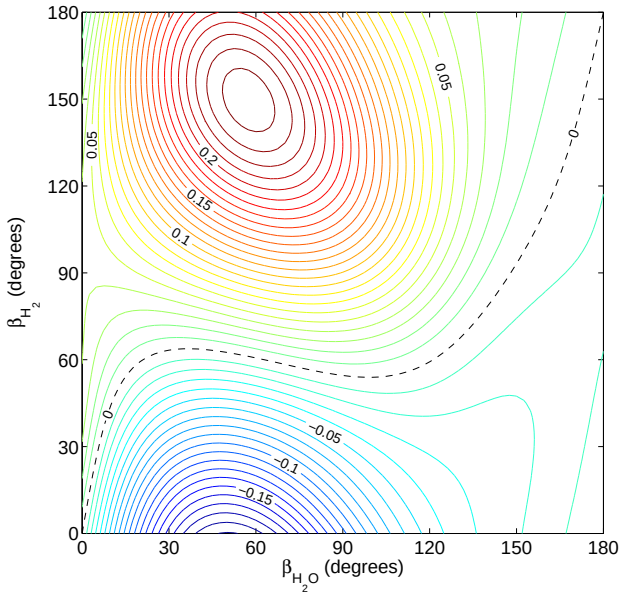
pH_2-oH_2O



oH_2-pH_2O



oH_2-oH_2O



Binding energies

Potential well depth $D_e = 235$ cm^{-1}

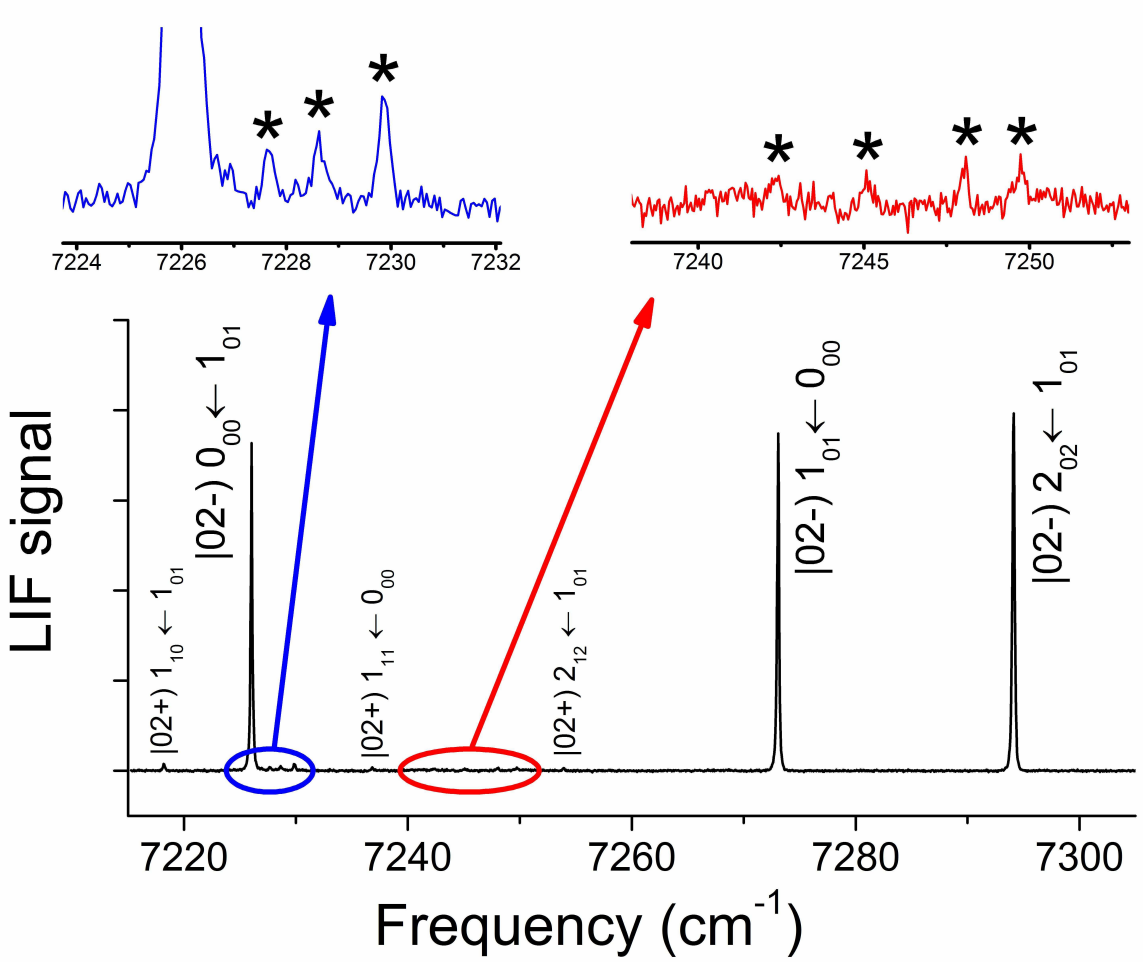
Dissociation energies D_0

para H_2 - para H_2O	33.6 cm^{-1}
para H_2 - ortho H_2O	36.6 cm^{-1}
ortho H_2 - para H_2O	53.6 cm^{-1}
ortho H_2 - ortho H_2O	59.0 cm^{-1}

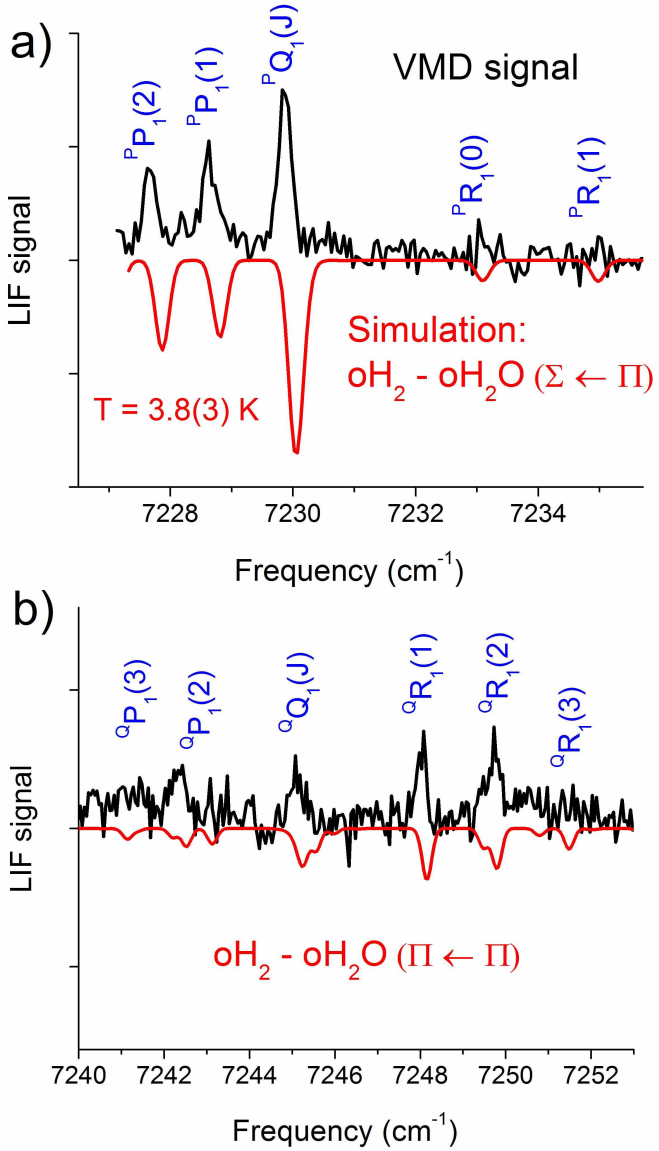
Selection rules

- H_2O $|02^-)$ odd under P_{12}, $|00^+)$ ground state even
- Overall dipole moment function even under permutations P_{12}, P_{34}, odd under inversion $E^* \Rightarrow$ symmetry A_1^-
- $|02^-) \leftarrow |00^+)$ transition dipole function depends on intermolecular coordinates and has symmetry A_2^-
- Pure $|02^-) \leftarrow |00^+)$ vibrational transition is forbidden
- Must be accompanied by internal rotor transition in the complex
- Sensitive to anisotropy of the intermolecular potential

H_2-H_2O $|02^-) \leftarrow |00^+)$ excitation spectrum



Spectrum simulated from calculated levels and line strengths



Also predissociation dynamics

(lifetimes)

can be understood from

the relative stability of

different ortho/para H_2 and

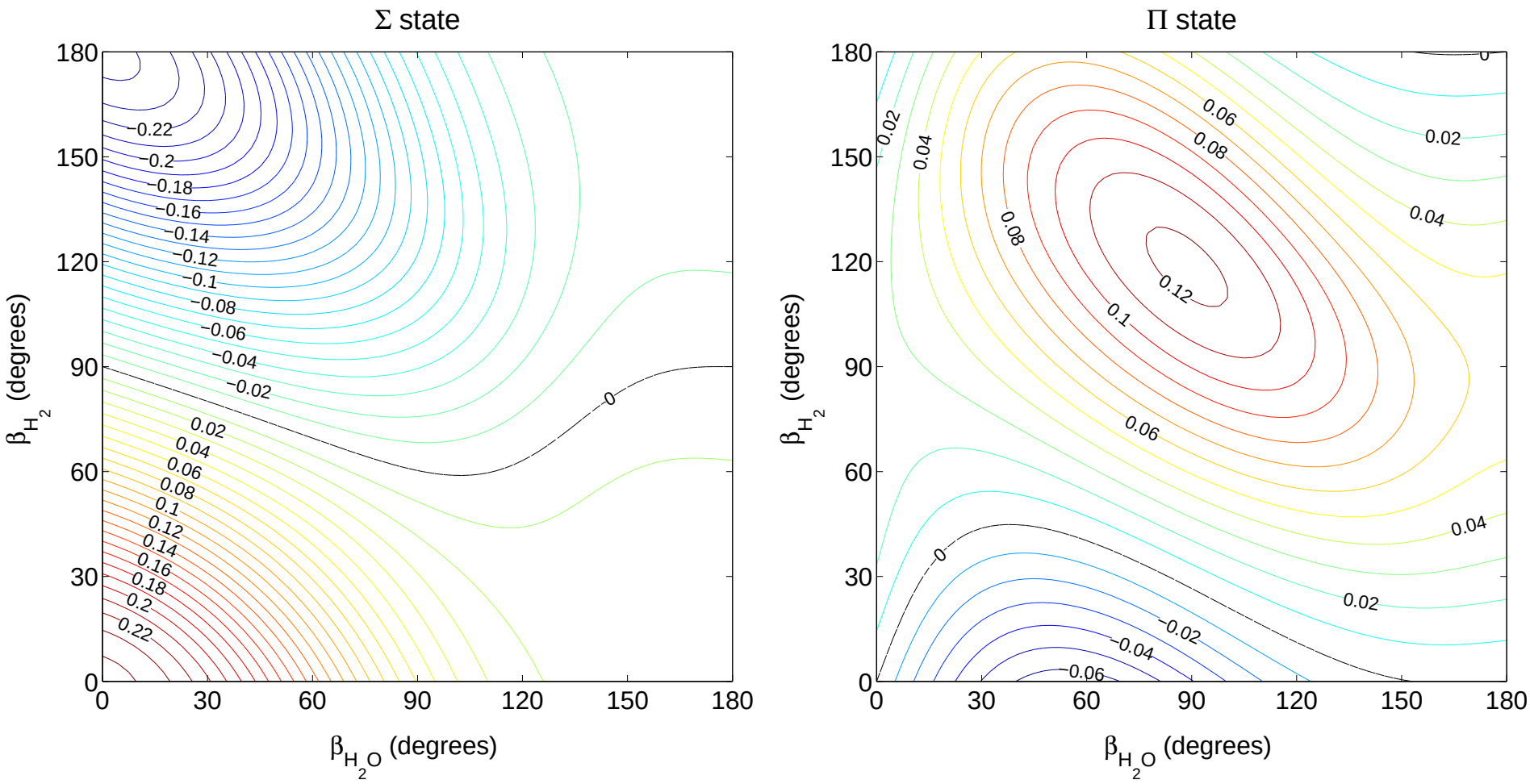
ortho/para H_2O species

and the nature of

the excited state

wave functions

Wave functions of oH_2-oH_2O $|02^-)$



For details, see:

J. Chem. Phys. (2012), the paper was accepted yesterday.

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